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Determination of mercury and its fractionation products in samples from legacy use of mercury amalgam in gold processing in Randfontein, South Africa

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ABSTRACT

This study aimed at determining the levels of total mercury (THg) in tailings dams, soil, sediments and water samples collected in the vicinity of legacy mercury amalgam gold mines. Acid digestion was employed in sample digestion followed by analysis using CVAAS. Tailings dams, community and garden soil, and stream sediments were further investigated for mercury fractions using a five step sequential extraction procedure. The concentrations of THg in tailings dams, community and gardens soil were 0.890–6.755 μg/g, 0.431–0.968 μg/g and 0.471–1.019 μg/g, respectively and the concentrations of THg in the sediments obtained from tailings dams, streams and wetlands were 0.649–1.998 μg/g, 0.604–1.356 μg/g and 0.681–1.356 μg/g, respectively. The concentrations of THg, in aqueous samples obtained from tailings, streams and wetlands were 0.032–0.070 μg/l, 0.004–0.068 μg/l and 0.007–0.012 μg/l, respectively. The sequential extraction procedure showed that most Hg in the tailings dams was largely elemental Hg and Hg bound to sulphur. Soil and sediments were largely dominated by organic bound Hg. Moderate seasonal correlation was observed in tailings dams soil, but weak seasonal correlation in soils collected in the vicinity of tailings. However, a strong seasonal correlation was observed in sediments and water samples. The concentrations of Hg obtained largely existed in organic and sulphate bound Hg and there is elevated potential to methylate Hg.

1. Introduction

Mercury (Hg) is one of the first elements with an in-depth study of its speciation or fractionation products [1]. The presence of Hg in the environment comes from two major sources, namely natural and anthropogenic. Its pristine concentration varies between 0.080 and 0.400 μg kg^{-1} in rocks, sediment or soil samples [2]. Native Hg is rare in nature, but it usually appears as complex sulphides with Mn, Zn, Fe, and other metals in the Earth's crust [3]. Global anthropogenic inputs of Hg into the environment were estimated at about 3.2–30 × 10^6 kg $year^{-1}$, whereas global natural Hg emissions were considered to be 3 × 10^6 kg $year^{-1}$ [4,5]. The first health effects of Hg manifested in the early 1950s in Japan after Hg contaminated fish were consumed. Related Hg food poisoning incidences have also been reported in Iraq and Nigata [2]. In view of these incidences, the United Nations through the United Nations Environment Programme (UNEP) endorsed the Minamata Convention on Mercury.

Gold mining is one of the major minerals mined globally and it is one of the major sources via which Hg gets into the environment, particularly when Hg amalgam is used during the recovery of gold from its ores [4]. Hg amalgam was widely used in the past to recover gold from its ores until about 1920 in the Witwatersrand basin, South Africa [5]. This method has since been replaced with the cyanidation process. However, the resulting wastes from the Hg amalgam processes were dumped on next available empty lands. In South Africa, gold mine tailings dams occupies large areas (about six billion cubic meters) and are located near communities which may be affected by Hg released through erosion processes [6]. By

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law, the tailings dams are supposed to be vegetated in order to prevent wind and precipitation erosions. However, pollution still remains in the tailings dams since a number of these dams have not been re-vegetated.

Hg levels in various environmental compartments have been studied in South Africa [7–18]. However, information on Hg concentrations on gold mine tailings dams was non-existent until the studies conducted by Lusilao et al. [5,19,20]. Although the aforementioned studies by Lusilao were on tailings dams and their immediate matrices, the studies did not give much attention to the fractionation of Hg in soils and sediments in communities located in the vicinity of gold mine tailings dams. Furthermore, the aforementioned study [19] used a four-staged fractionation method which is not exhaustive enough to isolate the different fractions. It is pertinent to point out that generally, most studies to date on Hg have not been conducted along with other anions and trace metals. This aspect is extremely important since these parameters have the potential to influence the behaviour, mobility and bioavailability of Hg in the environment.

Therefore, this study aimed at determining THg and its fractions and association with trace metals and anions in order to understand the fate, mobility and distribution of Hg within the legacy amalgam gold mining affected environment. Sequential extraction was used to examine operationally defined fractions of Hg in tailings dams, soil and sediment samples. Furthermore, seasonal distribution of levels of Hg in soil, sediments and water samples collected from gold mine tailings dams and its immediate surrounding areas in Randfontein, South Africa are presented. It is envisaged that this study will provide the benchmark on the fractionation and seasonal variation of Hg within gold mining environment where Hg amalgam was previously used for the extraction of gold from its ores as well as highlight Hg association with other trace metals and anions.

2. Materials and methods

2.1. Standards, reagents and apparatus

2.1.1. Standards and reagents

All the reagents used were Hg free and were, supplied by Sigma-Aldrich (Germany). Sulphuric acid (95–98%), hydrochloric acid (37%), nitric acid (70%), potassium permanganate (≥99%, low in Hg), potassium persulphate (≥99%), sodium chloride (≥99%) and hydroxylamine sulphate (99%) were used throughout the experiments. Aqueous tin chloride prepared from tin (II) chloride dihydrate (≥98%) was used to reduce the oxidised Hg to elemental Hg which was subsequently vaporised into the instrument for analysis. To digest the samples for trace metal determination, some of the above mentioned acids (nitric acid, hydrochloric acid) and 30% hydrogen peroxide (H_2O_2) from SSM Instruments (Pty) Ltd (South Africa) were used. Ultra-pure water prepared in our laboratory using SG Series Compact purchased at Evoqua water technologies (United Kingdom) was used throughout the experiment. Standard solutions of Ag, Al, Au, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Zn standards for AAS supplied by FLUKA Analytical (Switzerland) and Pb standard supplied by MERCK (Germany) were used throughout the experiments. For anions multi-element standard VII (Merck, Germany) and certified multi-anions standard solution PRIMUS (Fluka, Switzerland) containing F^-, Cl^-, Br^-, NO_3^-, SO_4^-, PO_4^- were used to calibrate the instrument and spiking.

All the glassware used were thoroughly washed with detergent, rinsed with tap water, soaked overnight in 10% HNO_3, rinsed three times with de-ionised water and dried in a clean oven at ±95 °C overnight.

2.2. Sampling area and sample collection

Randfontein is located South-west of Johannesburg (30 km West), in Gauteng Province South Africa. Some of the major and oldest gold mines in South Africa are located in Randfontein, where majority of the mines that operated before 1920 employed amalgam process as means of extracting gold from its ores. Fig. 1 shows the study area and sampling points.

Twenty five (11 soil, 7 sediments and 7 water) samples were collected from legacy amalgam tailings dams and their surrounding areas in winter (June) and summer (December) periods in 2015. Soil was collected at 5 cm depth (after clearing the debris) using acid-washed stainless steel trowel, placed in Ziploc bag and later in a sampling cooler bag. Water samples were collected by dipping thoroughly acid washed Teflon plastic-container 5 cm below the water surface. The precautions as prescribed by the USEPA Method 7471B and 245.1 for sampling procedures were carefully employed throughout the sampling processes [21,22]. The collected samples were transported to the laboratory and refrigerated until treatment and analysis commenced.

2.3. Sample preparation and digestion

Soil and sediment samples were air dried for ±24 h. The dried samples were gently macerated to separate the lumps and sieved with a stainless steel sieve of different sizes ranging from 45–630 μm. The fractions were subsequently subjected to particles size analysis using Microtrac S3500. Samples of <45 μm were used for all other analysis of soil and sediments. For THg analysis, acid digestion procedures for preparing solid, semisolid and water samples for analysis of Hg using CVAAS as outlined in USEPA methods 7471B and 245.1 were employed, respectively [21,22]. Briefly, macerated, sieved and thoroughly homogenized samples without applying intense force to break large particles were used. A 1 g of soil was weighed and carefully transferred into a 250 ml round bottom flask. Working under the fume hood and treating each sample individually, 10 ml of ultra-pure water was added. This was followed by the addition of 5 ml of aqua regia (3:1). The flasks were then sealed with aluminium foil to prevent any loss of Hg vapour and heated for 2 min at 95 °C in a heating mantle. The mixture was allowed to cool down after which 50 ml of ultra-pure water added. This was followed by the addition of 15 ml of freshly prepared potassium permanganate solution. The set-up was left for 15 min to allow for complete oxidation of Hg. For water samples, 100 ml was used and 8 ml of potassium persulphate added. Thereafter, the flasks were mounted with condensers and were sealed with aluminium foil to prevent any potential loss of Hg vapour. All the flasks were covered with glass wool within the heating chamber to ensure even distribution of the applied heat. The samples were then heated for 3 h, cooled and finally, 6 ml of sodium chloride-hydroxylamine hydrochloride added to reduce excess potassium permanganate. The samples were then made up to the 250 ml mark and kept in the refrigerator until instrumental analysis.

Sequential extraction described by Bloom et al. [23] was used to further investigate the fractions of Hg in soil and sediments. Samples analysed using this technique was frozen to minimize changes on Hg fractions prior to commencing with sample preparations. Briefly, soil samples collected from tailings dams, community, garden and sediments samples were sequentially leached with five extraction solutions shown in Table 1. For each extraction step, 50 ml of the extraction solution was added to 1 g of sample placed in a conical flask, sealed and shaken end-over-end at 250 rpm for ±24 h. The obtained decant was centrifuged at 3000 rpm for 15 min, and the aqueous solution was filtered through a Whatman 0.45 μm filter paper. The same extraction solution was used to rinse

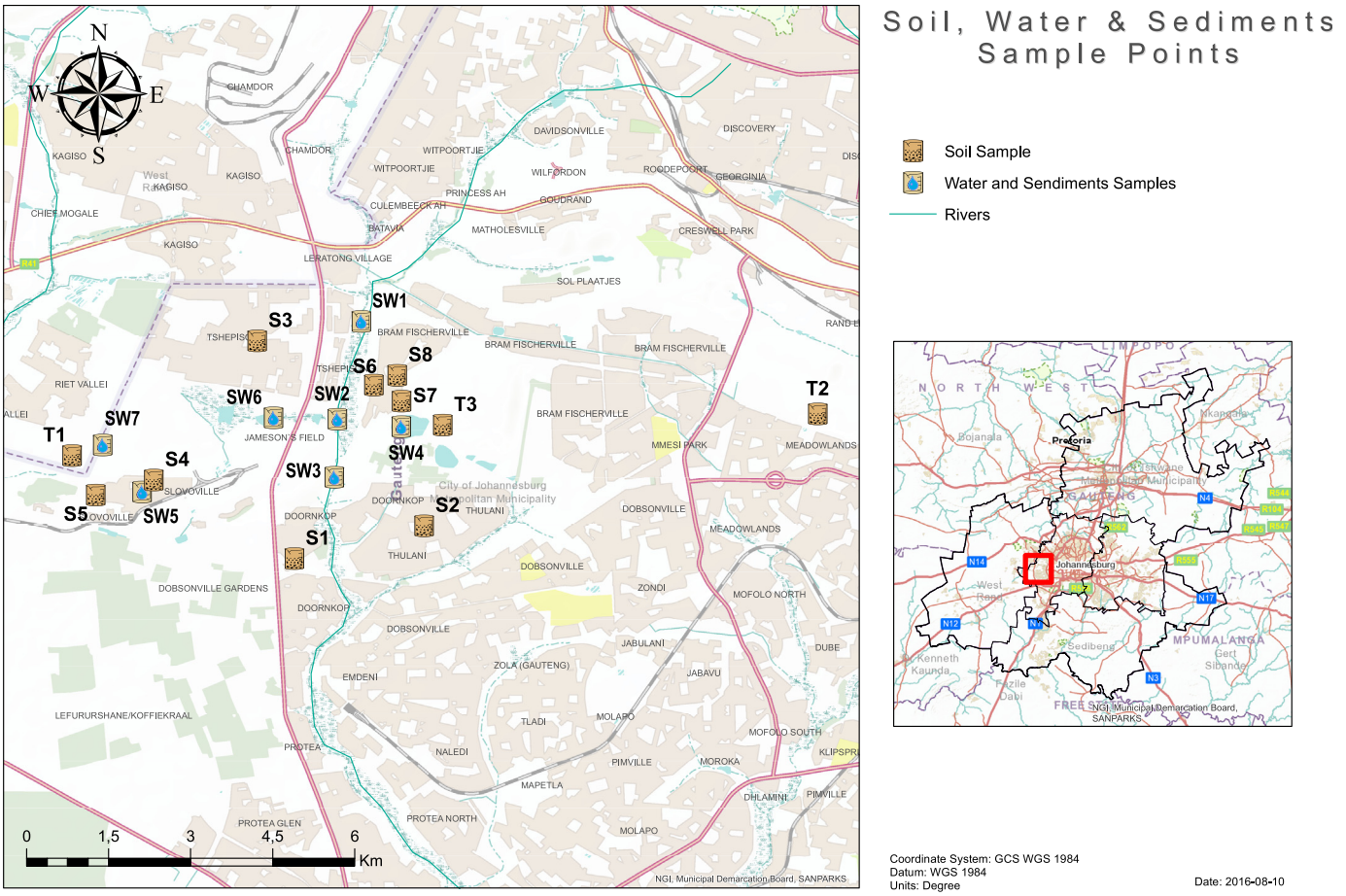

Fig. 1. Map of the study area showing sampled locations in Randfontein, Gauteng, South Africa.

Table 1
Sequential extraction procedures [23–25].

Fraction	Extracting solution	Extraction process	Operationally defined fraction	Potential Hg species
F1	DI water	Shaken in a water bath for ±24 h	Ion-exchangeable Hg	$HgCl_2$, $HgSO_4$
F2	0.1 M CH_3COOH +0.01 M HCl		Acid soluble Hg	HgO, Hg sorbed to oxides (Fe, Mn)
F3	1 M KOH		Organic matter bound Hg	Hg-organic, Hg_2Cl_2
F4	12 M HNO_3		Elemental Hg	Hg (0), Hg_2Cl_2 m-HgS w/inpurities
F5	Aqua regia	Acid digestion	Sulfide Hg	HgS, m-HgS

the aliquot and centrifuge vials, and thereafter re-shaken, re-centrifuged and added to the same filtrate solution. These steps were repeated for fractions 1–4. After adding 5 ml of aqua regia, 3:1 solution during the last stage (F5), the samples were heated at 95 °C for 2 h in a water bath to facilitate digestion. About 10 ml of prepared 0.2 N bromide monochloride solution was added as an oxidant.

For the determination of anions, the USEPA method 300.0 was employed [26], where a 1 g soil and sediment sample was placed in a beaker and 100 ml of de-ionised water added and stirred with a magnetic stirrer for 15 min. Thereafter, the sample was filtered through a Whatman filter paper and finally through a 0.45 μm syringe filter. A similar filtration process was employed for water samples. A portion of the unfiltered soil and sediment samples was used for the pH determination. To determine trace metals, acid digestion procedure for preparing soil samples for analysis of trace metals by Flame Atomic Absorption Spectrometry (FAAS) outlined by USEPA [27] was applied. About 1.5 g of soil and sediments was weighed and carefully transferred into a 250 ml conical flask (and 100 ml was used for water samples). About 10 ml of de-ionised water and HNO_3 were added and heated at ±95 °C using a hot plate without boiling for 15 min. Sample was then allowed to cool before an adding 5 ml of HNO_3 and heated initially for 30 min to achieve total decomposition and further heated for 2 h without boiling. The set-up was then allowed to cool down to room temperature. After cooling, 2 ml of de-ionised water and 3 ml of HCl was added. Thereafter, 1 ml (x3) of H_2O_2 was added consecutively to minimize the effervescence, and then heated for 2 h without boiling and thereafter allowed to cool. After cooling, the sample was filtered into a 100 ml graduated volumetric flask and filled with de-ionised water to the graduation mark while rinsing the filter paper. All experiments were performed under the fume hood.

2.4. Quality assurance

Certified reference material for Hg (CRM 024–050, purchased from Industrial Analytical Pty) was used to validate the method, and an average recovery of 109% ± 3.3 was obtained. Adequate care

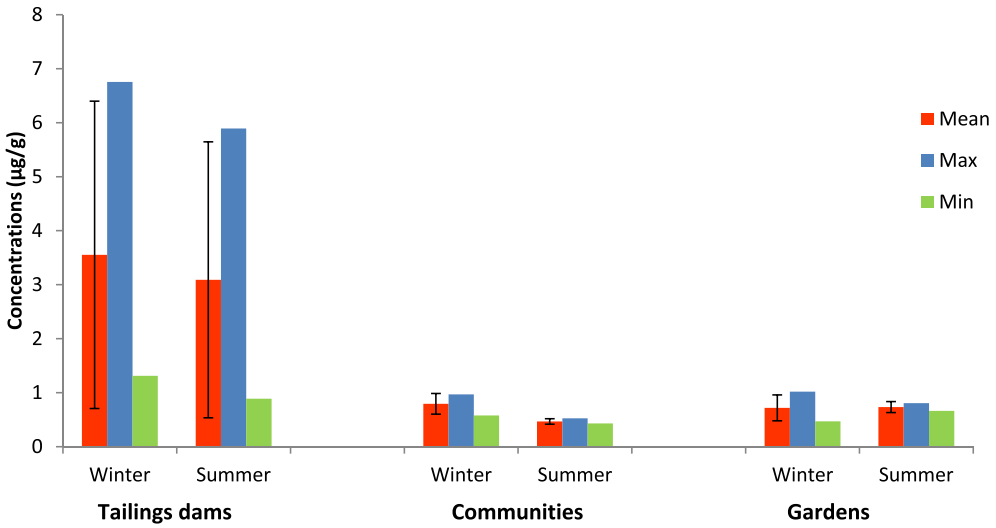

Fig. 2. Comparison and seasonal variation of concentrations of THg in soil samples from tailings dams, community and garden soils.

was taken to avoid carryover by running ultrapure water and reagent blanks in between samples. Also adequate care was taken to reduce the loss of Hg during sample preparation and analysis. For trace metals and common anions analysis, a quality check was conducted by spiking known amounts of certified standard into leached soil and ultra-pure water. An undigested 1 g of leached soil and 100 ml of ultra-pure water were spiked with 5 µg/l and 1 µg/l of trace metals respectively.

2.5. Data analysis

All the samples were prepared in triplicate and from the triplicate measurements the average and standard deviations were calculated. Statistical analysis to test for variations and relationships of concentrations were calculated using Microsoft office excel 2010.

3. Results and discussion

3.1. Total mercury

The instrument limit of detection (LOD) was 0.007 µg/g and limit of quantification (LOQ) was 0.022 µg/g, these were calculated based on the standard deviation of blanks and the slope of the calibration curve. The average recoveries of Hg on spiked leached soil sample and ultrapure water was 114% ± 6.6 and 112.5% ± 4.7, respectively. Figs. 2–4 show the concentrations of THg and seasonal variation in soil, sediments and water samples, respectively. All samples were measured in triplicates and the averages are presented. The tailings dams exhibited the highest concentration of THg ranging from 0.890–6.755 µg/g. As can be seen in Fig. 2, the concentration of THg in community and garden soil collected near the vicinity of the tailings dams ranged from 0.431–0.968 µg/g and 0.471–1.019 µg/g, respectively. In South Africa, Lusilao et al. [19], reported THg concentrations from legacy amalgam gold mine tailings dams that ranged from 0.005–2.581 µg/g and 0.001–0.100 µg/g in soil and sediments, respectively. The concentrations of THg obtained in the present study from community and garden soils are within the range reported by Lusilao et al. [19], although Hg found in sediments was higher.

As can be seen in Fig. 3, THg in sediments, 0.649–1.998 µg/g, collected near tailings dams were higher than those collected from nearby streams 0.604–1.356 µg/g and wetlands 0.681–1.356 µg/g, with concentrations. The concentration of THg in sediment samples collected from tailings dams was higher in winter (1.324 µg/g) than

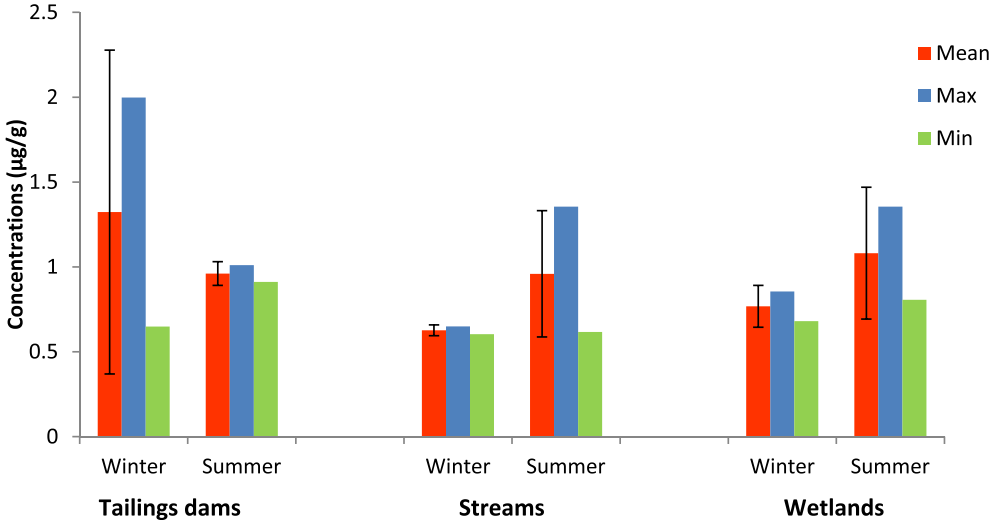

Fig. 3. Comparison and seasonal variation of concentrations of THg in sediment samples obtained from tailings dams, streams and wetlands.

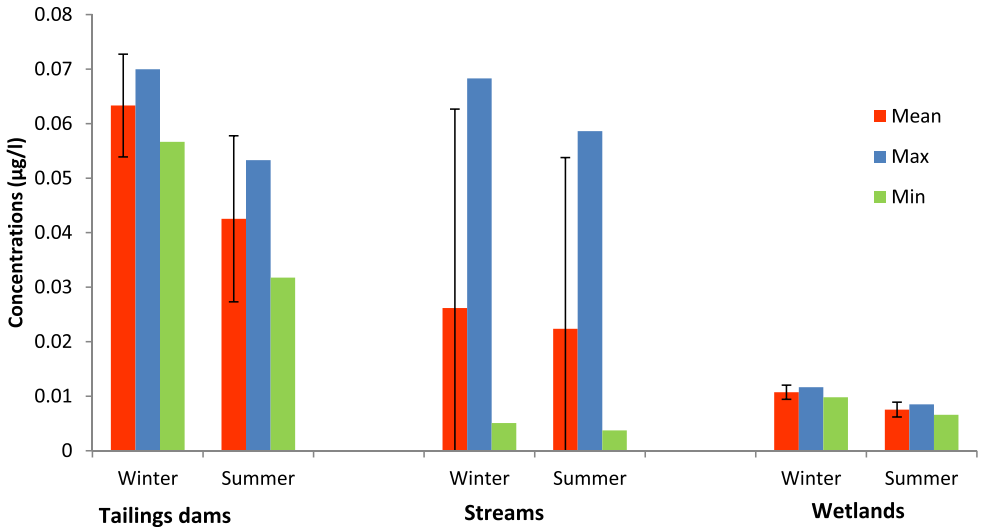

Fig. 4. Comparison and seasonal variation of concentrations of THg in water samples obtained from tailings dams, stream and wetlands.

in summer (0.961 µg/g) (Fig. 3). However, in stream and wetland sediments the concentrations of THg were elevated than in community and garden soil, and in stream and wetland water samples. This may be attributed to increased deposition of runoff eroded Hg on sediments. Sediments are an important sink and source of Hg release into water bodies and are considered as the main production site for methylmercury [28].

The concentrations of THg in water from tailings dams, streams and wetlands samples were 0.032–0.067 µg/l, 0.004–0.068 µg/l and 0.007–0.012 µg/l, respectively (Fig. 4). In South Africa, Lusilao et al. [19], reported the concentrations that range from <0.001–0.221 µg/l of THg in water near legacy amalgam gold mines. The concentrations of THg in water obtained in the present study from tailings dams, streams and wetlands are within the range of concentrations found by other studies [19]. The concentrations obtained were also close to the values from other studies conducted at different regions in South Africa [20]. Generally, all studies conducted so far from different regions in South Africa have confirmed the presence of Hg in legacy amalgam tailings dams and these may pose health threat to the communities living within the vicinity of the tailings dams.

As shown in Figs. 2–4, the concentrations of THg across all the samples in general indicated higher concentrations in winter than in summer. Similar trend has also been reported [20,29]. The observed higher concentrations observed in winter than in summer may be attributed to decreased wind and runoff erosion mechanisms in winter compared to summer. However, stream and wetland sediments showed higher concentrations in summer that in winter, this might be attributed to increased runoff deposition on sediments during summer than in winter season (Fig. 3). The concentrations of THg, in aqueous samples obtained from tailings, streams and wetlands were higher in winter than in summer season (Fig. 4). This may be attributed to elevated stream-flow during summer. There was a strong seasonal correlation in tailings dams soil ($r = 0.995$), and weak correlation ($r = 0.295$ and $r = 0.325$) in community and garden soil. The variation of seasonal correlation on tailings dams, community and garden soil may be attributed to the fact that physiochemical conditions of a particular location can be different, hence they can behave differently. For example, Hg in contaminated sandy soil is easily leached and eroded compared to contaminated clay soil. The concentrations of THg obtained around communities, garden and wetlands exceeded the recommended limits set by South African government department. The recommended limit for community and garden soil is 1.000 µg/g [30]. The recommended limit for THg in drinking water is 0.040 and on stream and wetland water is 1.000 µg/l, respectively [31]. The Canadian Council of Ministry of the Environment has set the possible exposure limit for THg in sediments at 0.700 µg/g [32]. It is evident that the majority of the THg concentration determined in soil, water and sediment in the present study exceeded these limits.

3.2. Fractionation of mercury

Hg fractionation is important because it provides an understanding on the distribution of compounds and their interaction with physiochemical characteristics of the area that determines the toxicity, environmental mobility and bioavailability [24]. The aforementioned Table 1 shows different fractions of Hg, operationally defined fractions and possible compounds of Hg to be extracted by different extraction solutions used. Fig. 5, shows fractions of Hg on two tailings dams (Tailing dam one (T1) and Tailings dam two (T2)), community soil (soil one (S1)), garden soil (soil two (S2)), and stream sediments (sediment one (Sed1) and sediment two (Sed2)). The operational fractions of Hg varied in different samples. F4 and F5 were the dominant fractions on tailings dam T1 and T2 ranging from 38.7–43.1% and 17.7–50.4%, respectively. In contrast, soil and sediments were dominated by F3. On community and garden soil, F3 ranged between 36.1-52.2% and 23.6–35.6%, respectively. Extracts of F3 fractions are likely to be associated with organic materials and may limit the mobility and bioavailability of Hg under certain conditions [25,33]. The current results are in agreement with the study conducted by Yuan et al. [34]. Hg bound to organic matter (F3) is also classified as semi-mobile and semi-bioavailable fraction which is greatly mobilized as a result of digestion by organisms [34]. Liu et al. [33] suggested that F3 could include methylmercury and is strongly correlated with methylation potential and plays an important role in biochemical cycling of Hg under certain conditions. Hence, sediments are known to be favourable sites for methylation of methylmercury [28]. F4 accounted for the majority of the fraction in a study that was conducted on gold mine affected sediments in Brazil [35]. The results of this study are also in agreement with the study conducted on tailings dams and adjacent soils by Bloom and Katon [24]. Losilao et al. [19], conducted Hg fractionation using a four

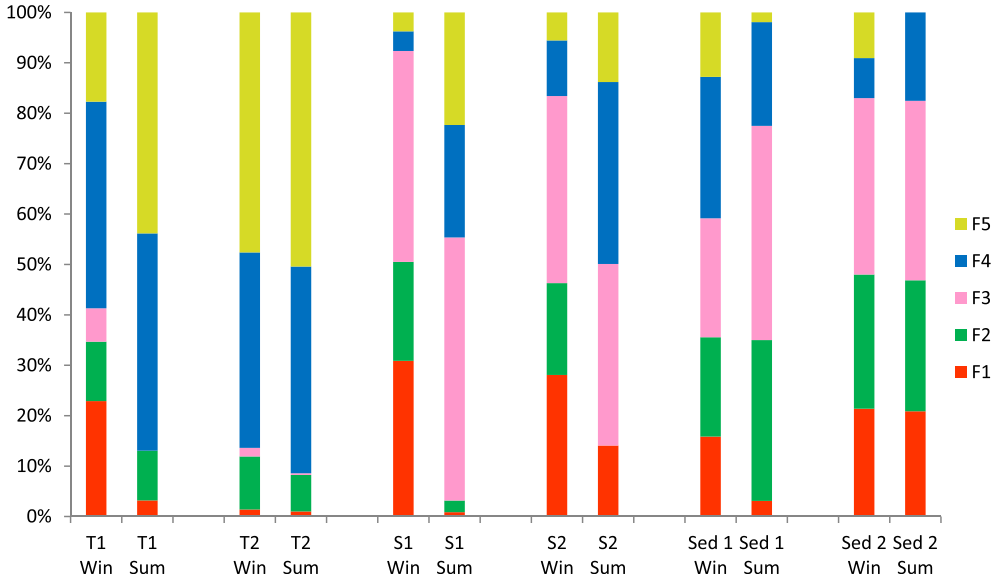

Fig. 5. Seasonal variation of fractions of mercury in soil and sediment sample (F1 = water soluble, F2 = weak acid soluble, F3 = organic bound, F4 = elemental, F5 = sulphide bound, T1 and T2 = tailings dams soils, S1 = community soil, S2 = garden soils, Sed1 and Sed2 = stream sediments, Win = Winter, Sum = Summer).

staged sequential extraction process. They found residual fraction representing 91.3–94.6% of THg in soil samples. Recent study on gold mining sediments found organic bound Hg the highest at 48% followed by F4 at 26%, F5 at 18%, F2 at 4.7% and F1 at 1.7%, respectively [36]. In the same study, Hg was found at elevated concentration in the fractions at different matrices. The authors also suggested that Hg fractionation may be influenced by physiochemical characteristics which are largely site specific [19]. On average, there was a moderate seasonal correlation of r = 0.613 on T1 and T2, respectively. Tailings dams sediments showed moderate seasonal correlation of r = 0.724 and r = 0.899 on Sediment 1 and 2, respectively. However, there was a weak seasonal correlation on community and garden soil of r = 0.311 and r = 0.323, respectively.

The operational fractions provided more evidence that Hg distribution and mobility vary seasonally due to influences such as sulphide and iron content, organic matter and precipitation. The results demonstrated that most Hg in the studied tailings dams soil samples was stable with low bioavailability potential. The results also indicated that there is elevated methylation potential in community soil and sediments as a result of dominant organic bound, acid soluble and water soluble Hg. Sequential extraction procedure indicated that it is not enough to evaluate the fate, mobility and behaviour of Hg only by THg determination, hence it has been useful in providing an insight of the potential health and environmental risks. It should be noted that the extraction solutions employed during sequential extraction are not selective enough and some fractions could contain other similar chemical species [19,24]. For example, HNO_3 could possibly liberate a certain amount of mercuric sulphide (HgS).

3.3. *Potential influence of anions and trace metals on Hg fractionation*

The concentrations of selected anions, trace metals in tailings dams, in the study area determined along with THg are presented in Figs. 6–7. Their determination along with THg was deemed

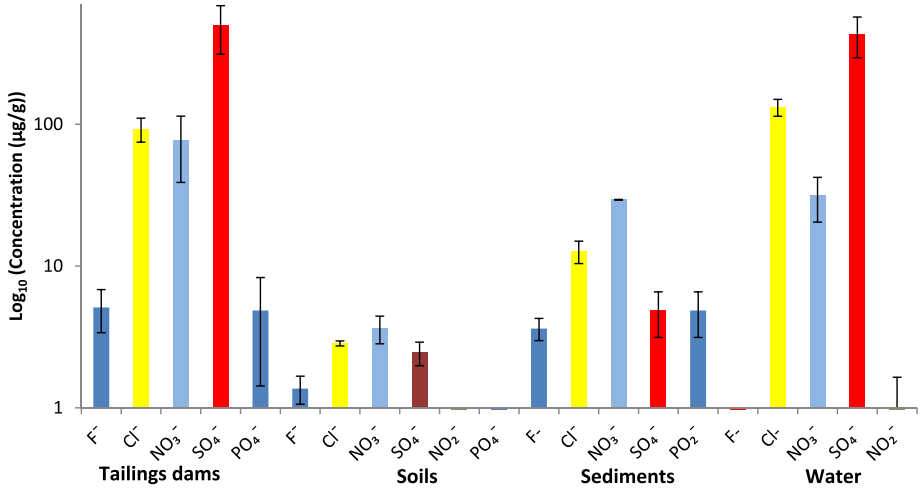

Fig. 6. Average concentrations of anions in soil, water and sediment samples as.

necessary since these parameters have the potential to influence the behaviour, mobility and bioavailability of Hg in the environment. Hence, fractionation of Hg largely depends on these physiochemical constituents of the environment. For example, the pH determined in the tailings dams ranged from 3–4. At this pH, soluble Hg compounds can be dissolved thereby releasing Hg [9]. Elevated pH increases the concentration of negatively charged hydroxyl ions (OH^-), which might attract and retain divalent mercury [37]. Whereas, low pH is characterised by high positively charged hydrogen (H^+) ions which play a direct role in several reactions, hence reaction rate is pH dependent [38]. For example, under neutral or alkaline conditions, the Fe^{3+} is precipitated as ferric oxide or oxyhydroxide. This reaction releases H^+ ions into the environmental solutions that further reduce other Hg containing compounds [38]. Moreover, at low pH ranging from 1–3.5, stable compound such as HgS are soluble and are dissociated. Hydrolysis of mercury increases with increasing pH, and mercuric (II) hydroxide ($Hg(HO)_2$) has been reported to be increasingly adsorbed by soil constituents from pH 5–9 [39].

As can be seen in Fig. 6, sulphate had the highest concentrations ranging from 0.952–500.000 μg/g 0.846–2.445 μg/g, 4.854–29.382 μg/g and 157.863–432.856 μg/l for tailings dams, soil, sediment and water samples, respectively. Incidentally, the soil and sediment samples collected from the tailings dams generally had the highest concentrations. Interestingly, water samples did not show the same trend, although exhibited higher sulphate concentrations than those obtained in soil and sediment samples. The sulphate levels obtained in the current study have a number of potential effects on the mobility, toxicity and bioavailability of mercury in the environment. First, Hg could bind with sulphur to form mercuric sulphide, which is a stable and less soluble compound. Consequently, Hg can be immobilized in the environment for an extended period if it binds to the compound under normal conditions. Second, the sulphate-rich mineral in tailings dams could support the growth and survival of sulphate-reducing bacteria, which play an important role during the methylation of Hg into methylmercury. Under anaerobic conditions, sulphate-reducing bacteria are the major groups involved in methylation of species into methylmercury [40]. By so doing, the presence of sulphate could trigger the conversion of Hg from its less toxic forms into its most toxic form.

The determined chloride concentrations ranged from 2.061–92.770 μg/g, 2.277–2.847 μg/g, 2.087–12.706 μg/g and 50.582–132.093 μg/l for tailings dams, soil, sediment and water samples, respectively. Chloride is known to have several influences on the mobility, toxicity and bioavailability of in the environment. For instance, the oxidation of Hg is highly dependent on the amount of chlorine present and less on the amount of other anions such as bromide and fluorine [41]. Furthermore, chloride concentration of 20.000 μg/g can influence the mobility of Hg because they have high affinity for Hg to form mercuric chloride ($HgCl_2$). $HgCl_2$ is highly soluble and can compete with hydroxide ions (OH^-) and other organic ligands for Hg binding [37]. The solubility and affinity of Hg compounds determines their concentration and mobility in the environment. Mercuric salts such as $HgCl_2$, HgS and mercury (I) hydroxide ($Hg_2(OH)_2$ vary widely in solubility. For example, $HgCl_2$ is readily soluble in water, while the HgS is insoluble but soluble at pH less than 3.5 [42]. Bromide (Br^-) and fluoride (F^-) have also been shown to influence Hg speciation mainly because they act as ligands in complexation reactions [43]. In this study, the observed nitrate (NO_3-) concentrations were relatively low and they ranged from 0.164–76.568 μg/g, 0.476–3.630 μg/g, 0.400–76.568 μg/g and 0.102–31.326 μg/l on tailings dams, soil, sediment and water, respectively. In contrast, (NO_3-) concentrations in water were relatively lower than in sediments. Incidentally, a similar trend was observed on nitrite (NO_2-), where concentrations ranged from 0.093–76.568 μg/g on tailings dams, 0.006–0.020 μg/g on soil and below detection limit on sediments and water samples. Presently, it is not yet clear if both NO_3- and NO_2- have any direct effect or influence on the mobility, toxicity and bioavailability of Hg in the environment.

Fig. 7 shows the determined concentrations of several trace metals. Not surprisingly, iron (Fe) had the highest average concentration possibly due to its natural abundance in the earth crust. The determined Fe concentrations ranged from 74.451–177.794 μg/g, 166.826–171.603 μg/g and 172.168–181.857 μg/g for tailings dams, community and garden soil, respectively. In sediments and water, Fe reached the highest concentrations of up to 1438.200 μg/g and 1452.130 μg/l, respectively. The presence of Fe at elevated concentration is known to have a great influence on the concentration of Hg and its speciation products in the environment. The presence of Fe can adequately enhance the effectiveness of certain iron-reducing bacteria since they can be oxidised to ferric (Fe(III)), which acts as a terminal electron acceptor that provides sufficient nutrients and energy to methylate Hg into methylmercury [44,45]. Under anaerobic conditions, similar to sulphate-reducing bacteria,

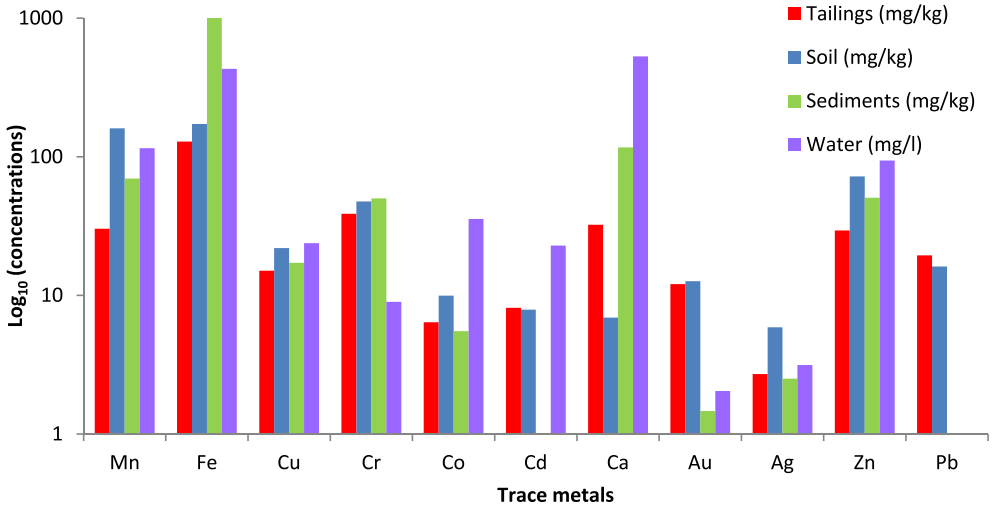

Fig. 7. Trace metal concentrations in tailings dams, soil, sediment and water samples.

iron-reducing bacteria can be actively involved in the methylation of Hg species [40].

Manganese (Mn) concentrations ranged from 0.197–65.072 μg/g, 80.628–259.739 μg/g and 101.025–238.528 μg/g for tailings dams, community and garden soil, respectively. Hg might be sorbed to oxides (Mn, Fe) to form Hg oxides, which is a weak acid soluble compound. Trace metals such as lead (Pb), uranium (U), silver (Ag), zinc (Zn), cadmium (Cd), copper (Cu), manganese (Mn), amongst others, which are common in gold ores and legacy amalgam affected areas can also compete with Hg for complexation. Hence, they might subsequently influence the mobility, toxicity and bioavailability of Hg in the environment.

4. Conclusion

This study has shown the presence of Hg in tailings dams, soil, sediments and water samples collected from gold mining area where Hg amalgam was used in gold extraction from its ores. The highest concentration was observed in the tailings dams compared to the other environmental samples. On the basis of collected data, it can be inferred that the legacy amalgam tailings dams are primary source of Hg contamination in the study area. Moderate seasonal correlation was observed in tailings dams soil, but weak seasonal correlation in soils collected in the vicinity of tailings. The majority of concentrations of THg determined were found to be above the recommended limits, and, therefore, it is of concern to surrounding communities. In general, the concentrations of Hg obtained in the present study largely existed in stable and less bioavailable forms such as organic and sulphate bound Hg. On the other hand, the concentrations determined in community, garden soil and stream sediments, appeared to have elevated potential to methylate Hg into the most toxic compound such as methylmenrcury was predominant. The sequential extraction procedure showed that most Hg in the tailings dams was largely elemental Hg and Hg bound to sulphur.

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